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Petroleum & Chemical
Research Dept.
Jersey City, N. J.



Report No. RL-55-442

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Petroleum and Chemical Research Department

PROGRESS REPORT

ARCTIC RUBBER

U.S. Army Contract DA-44-109-qm-1580
For the Period August - September 1955

December 1, 1955

Copy No. **15** Report RL-55-442

Petroleum and Chemical Research Department
Laboratory Division, Jersey City, N.J.



PROGRESS REPORT

Arctic Rubber - U.S. Army Contract DA-44-109-qm-1580

Subject: for the period August - September, 1955

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Period Covered: August - September, 1955

L.O. No. D-221; Job No. 5675

Previous Reports on this Subject:

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| RL-51-146 | " February 1, 1951 |
| RL-51-156 | " April 1, 1951 |
| RL-51-163 | " July 1, 1951 |
| RL-51-174 | " October 1, 1951 |
| RL-52-183 | " February 1, 1952 |
| RL-52-195 | " May 1, 1952 |
| RL-52-209 | " August 1, 1952 |
| RL-52-248 | " October 1, 1952 |
| RL-53-259 | " January 1, 1953 |
| RL-53-274 | " April 1, 1953 |
| RL-53-289 | " August 1, 1953 |
| RL-54-329 | " July 29, 1954 |
| RL-54-333 | " August 4, 1954 (Final Sum. Report- DA-44-109-qm-222) |
| RL-54-353 | " September 30, 1954 |
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| RL-55-401 | " April 1, 1955 |
| RL-55-422 | " July 1, 1955 |
| RL-55-434 | " September 1, 1955 |

E. F. SCHWARZENBECK

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I. Introduction

A. Purpose of the Project

The preparation of an oil and fuel-resistant rubber which retains its elastic properties over the range -70°F. to 160°F.; the development of a rubber suitable for use at 500°F.; the investigation and solution of the accompanying problems of monomer preparation, polymerization techniques, and polymer evaluation.

B. Research Program

To achieve this purpose, the Quartermaster Corps. has authorized the M. W. Kellogg Company to conduct a broad investigation of fluorine-containing polymers, which involves monomer synthesis, polymer preparation, and polymer testing.

Many of the monomers desired for investigation are unavailable commercially. In a few cases, these have been synthesized at M. W. Kellogg. Otherwise, the monomers or their precursors are prepared by Dr. Paul Tarrant of the University of Florida, and Dr. Aldrich Syverson of Ohio State University, or obtained on an exchange basis from the Minnesota Mining and Manufacturing Co. and the Polaroid Corporation.

Polymer preparation has received chief emphasis at M. W. Kellogg. The initial phase of this work is the exploratory copolymerization of each new monomer with selected monomers on hand. The results of screening tests on polymers so obtained are used in the selection of new monomer structures, more suitable monomer combinations and mole ratios, and better recipes and polymerization conditions.

Polymer systems exhibiting solvent swell resistance and low temperature characteristics comparable or superior to the chlorotrifluoroethylene-vinylidene fluoride copolymer originally developed on this project are investigated in greater detail. The more outstanding of these will be prepared in pound batches for a more thorough evaluation.

Polymer compounding, testing, and evaluation are conducted by Mr. C. B. Griffis, Angus Wilson, and staff at the Quartermaster Research and Development center at Natick, Mass. ASTM procedures D-471-52T (solvent swell), and D-1053-52T (Gehman Stiffness) are employed in screening the specimens obtained in the exploratory copolymerizations.

C. Past Progress

The copolymer systems investigated were 660, and the rubber-like systems, 332. (Refer to RL-55-434)

II. Summary of Current Progress

The number of monomers available for copolymerization is 84; the number of different polymer systems investigated, 686, and the number of rubberlike systems, 348.

The following monomers have been copolymerized with selected monomers now available: $\text{CF}_2=\text{CHCH}=\text{CH}_2$, $\text{CF}_2=\text{CFCF}_2\text{Cl}$ and vinyl pyridines.

The development of a new high temperature rubber $\text{CF}_2=\text{CF}_2/\text{CF}_2=\text{CFCF}_2\text{Cl}$ is in progress. The most promising copolymer systems remain to be $\text{CF}_2=\text{CH}_2/\text{CF}_3\text{CF}=\text{CF}_2$ and $\text{CF}_2=\text{CH}_2/\text{CF}_2=\text{CF}_2$.

III. Experimental Section

A. Total Monomers

Eighty-four monomers are now available for copolymerization study. (Refer to RL-55-434).



B. Chemicals Received

The following samples were received during the current period from the Ohio State University:

| <u>Compound</u> | <u>b.p., °C.</u> | <u>Amount, g.</u> |
|--|-------------------|-------------------|
| CH ₂ =CHOCF ₂ CHClF | 73-74/atm. | |
| CHCl ₂ CHClOCF ₂ CHClF | 86.5-87.5/30 mm. | |
| CH ₂ ClCHClOCF ₂ CHClF | 71-73/30 mm. | 25 |
| CH ₂ ClCH ₂ OCF ₂ CHClF | 80-82/100 mm. | |
| CF ₃ CCl ₂ OCF ₂ CF ₂ Cl | 90.5-90.7/741 mm. | |
| CH ₃ CF=CH ₂ | -22 to -21.5 | 1870 |

The following pyridines were purchased from Reilly Tar & Chemical Corp.:

| | | |
|-------------------------------|-------------------------|-------|
| 2-vinyl pyridine (monomer 83) | 79-82°/24 mm. | 1 lb. |
| 4- " " | (") 84) 70-74°/15 mm. | 1 lb. |

C. Monomer Purification

The crude CF₂=CFCF₂Cl (monomer 82) obtained by the decarboxylation of the sodium salt of C₄ telomer acid was fractionated. The major fraction (ca. 630 g.) boiled between 7-8.5°C., was collected. The mass spectrometric analysis indicates the monomer to be pure.

2 and 4 vinyl pyridine (monomers 83 and 84) were each fractionated under vacuum in order to remove inhibitor and impurities. The water-white purified monomers were stored under N₂ at -70°C.



D. Monomer Analysis

Mass spectrometric analyses of the three fluorinated butadienes received from Dr. Tarrant are as follows:

1. $\text{CF}_2=\text{CHCH}=\text{CH}_2$ (monomer 37)

| | <u>Mole % (app.)</u> |
|--|----------------------|
| $\text{CF}_2=\text{CHCH}=\text{CH}_2$ | ~70 |
| $\text{C}_4\bar{\text{H}}_5\text{F}_3$ | ~22 |
| C_5H_{10} | ~8 |
| $\text{C}_4\text{H}_4\text{F}_4$ | trace |

2. $\text{CF}_2=\text{CFCH}=\text{CH}_2$ (monomer 56)

This sample appears to be pure. (Water vapor is the only impurity noted).

3. $\text{CF}_2=\text{CHCF}=\text{CH}_2$ (monomer 51)

| | <u>Mole % (app.)</u> |
|---------------------------------------|----------------------|
| $\text{CF}_2=\text{CHCF}=\text{CH}_2$ | ~85 |
| $\text{C}_4\text{H}_4\text{F}_4$ | ~15 |

E. Polymer Preparation

Polymerization using 686 monomer systems has been attempted. The 26 new systems are: 1-82, 1-84, 2-10, 2-14-72, 2-84, 16-51-56, 16-51-74, 16-56-74, 21-32, 24-84, 37-42, 37-56, 37-72, 37-73, 37-74, 37-84, 51-82, 51-84, 56-82, 56-84, 74-82, 74-83, 74-84, 82, 82-84, and 84.

Of the systems investigated 348 can be considered rubberlike. The 16 new systems are listed below: 2-14-72, 16-51-56, 16-51-74, 16-56-74, 21-32, 24-84, 37-42, 37-56, 37-72, 37-73, 37-74, 51-82, 56-82, 74-82, 74-84, and 82-84.

Experimental data relative to the exploratory work carried out during the current period are set forth below:



1. Homopolymerization of Halogenated Propenes

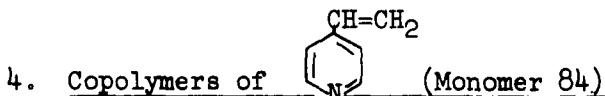
A few attempts to homopolymerize $\text{CF}_3\text{CF}=\text{CF}_2$, $\text{CF}_3\text{CCl}=\text{CF}_2$ and $\text{CF}_2=\text{CFCF}_2\text{Cl}$ (monomers 14, 32 and 82 respectively) in both solution and emulsion recipes failed to give high molecular weight polymers (see runs 3007-8, 3021-22, 3053 and 3060, Table I). In some cases small amounts of yellow oil or powder were obtained.

2. Copolymers of $\text{CF}_2=\text{CHCH}=\text{CH}_2$ (Monomer 37)

This monomer gives a powdery homopolymer. It copolymerizes with fluorinated dienes and propenes to give short rubbery products in good yields (see runs 3009-11, 3023-30, 3036-43, Table I).

3. Copolymers of $\text{CF}_2=\text{CFCF}_2\text{Cl}$ (Monomer 82)

This monomer does not homopolymerize in the regular emulsion recipe (see run 3053, Table I). However, it copolymerized with various fluorinated dienes and ethylenes giving rubbery polymers in good yields (see runs 3054-58, Table I and Table III).



This monomer gives a plastic homopolymer. It copolymerizes with fluorinated dienes, propenes and ethylenes giving colored resinous or stiff rubbery polymers (see runs 3012-23 and 3058, Table I) in good yields.

5. Exploratory Terpolymers

The Gehman T_5 value of the copolymer system $\text{CF}_2=\text{CHCF}=\text{CH}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$ was lowered six degrees by terpolymerizing the fluorinated dienes with a third monomer $\text{CH}_2=\text{CHOCF}_2\text{CF}_2\text{H}$ (see run 1979, Table II). A series of terpolymers (see runs 3035, 3044-47, Table I) have been made during this current period. They will be sent to QM for evaluation as soon as the analytical data are complete.

F. Polymer Evaluation

During the past two months the data of the low temperature flexibility and fuel resistant properties of 25 rubbery polymers were received from the Quartermaster Corps (see Table II).

Among the 25 copolymers, the following five samples: 1-51, 14-51, 18-51, 51-56 and 51-73 (see runs 1959, 1971, 1977, 1984 and 1999, Table II) have volume swells and torsional moduli comparable with X-300 Elastomer, but have better Gehman T₅ values. Different molar ratios of these copolymer systems will be prepared.

IV. High Temperature Rubber Program

The excellent thermal stability, fuel and acid resistance of the $\text{CF}_2=\text{CH}_2/\text{CF}_3\text{CF}=\text{CF}_2$ copolymers (see Table VIII, RL-55-434) have stimulated the copolymerization of other fluorinated propenes and butenes with vinylidene fluoride or other fluorinated ethylenes.

$\text{CF}_2=\text{CFCF}_2\text{Cl}$ (monomer 82) copolymerizes with $\text{CF}_2=\text{CH}_2$ to give rubbery products in good yield. The results of a few physical and chemical tests are summarized in Table III. Its resistance to "Esso Turbo Oil 15," the diester type hydraulic fluid, is poor. The tests for thermal stability and fuel resistance are now in progress, and will be reported when the data are available.

V. Plans for Future Work

1. Exploratory polymerizations of new monomers will continue with selected monomers, based upon past experiences.
2. Some theoretical work on the development of new monomer structures and methods of monomer synthesis is planned.
3. The reactivity ratios of $\text{CF}_2=\text{CHCF}=\text{CH}_2$ and $\text{CF}_2=\text{CFCH}=\text{CH}_2$ will be determined.
4. One pound batches of the appropriate molar ratios of the following systems: $\text{CF}_2=\text{CHCF}=\text{CH}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$, $\text{CF}_2=\text{CH}_2/\text{CF}_3\text{CF}=\text{CF}_2$ and $\text{CF}_2=\text{CH}_2/\text{CF}_2=\text{CF}_2$ will be prepared for evaluation of cured samples.
5. Preparation of ether-linked fluorocarbon polymers will be attempted.


E. S. LO

References to Original Records

Notebook No. 339, pp. 167-189 incl.
" " 308, pp. 176-180 "

TABLE I

EXPLORATORY POLYMERIZATION

| No. | Comonomers | Mole Ratio Charged /10/ | Polymerization Conditions | | | | % Conv. | Appearance of Sample /11/ | |
|--------------------|--|-------------------------|---------------------------|-----------|--------|----------------|-----------------------|---------------------------|--|
| | | | Time hrs. | Temp. °C. | Recipe | Before Milling | | After Milling | |
| 2097 | CF ₂ -CFC1 | 100 | 22 | | /1/ | 41 | Powder | - | |
| 2098 | " | 100 | 22 | | /2/ | 23 | Powder | - | |
| 2099 | " | 100 | 22 | | /3/ | 80 | Powder | - | |
| 3000 | CH ₂ -CPCH=CH ₂ | 100 | 22 | | /1/ | 96 | Short Rubber | Short Rubber | |
| 3001 | CH ₂ -CPCH=CH ₂ /CF ₂ -CPCH=CH ₂ | 50/50 | 22 | | /1/ | 84 | - | - | |
| 3002 | CF ₃ CCl=CH ₂ /CH ₂ -CPCH=CH ₂ | 50/50 | 72 | | /3/ | 45 | - | - | |
| 3003 | " /CH ₂ -CCH=CH ₂ | 50/50 | 72 | | /3/ | 28 | Soft Resin | - | |
| 3004 | " /CH ₂ -CFC1 | 50/50 | 72 | | /3/ | 1 | Low Mol.Wt. Polymer | - | |
| 3007 | CF ₃ CF=CF ₂ | 100 | 68 | 50 | /4/ | 0.3 | Powder | - | |
| 3021 | " | 100 | 48 | | /5/ | 1 | Powder | - | |
| 3008 | CF ₃ CCl=CF ₂ | 100 | 68 | | /4/ | 0.5 | Powder | - | |
| 3022 | " | 100 | 48 | | /5/ | zero | - | - | |
| 3009 | CF ₂ -CHCH=CH ₂ /CH ₂ -CHOCH ₂ CF ₂ H | 80/20 | 68 | | /3/ | 54 | Short rubber | Short rubber | |
| 3010 | " /CF ₃ CF=CF ₂ | 70/30 | 68 | | /3/ | 44 | Powder | - | |
| 3011 | " /CF ₃ CCl=CF ₂ | 70/30 | 68 | | /3/ | 40 | Rubbery powder | Short rubber | |
| 3023 | " /CF ₃ CH=CH ₂ | 70/30 | 25 | | /6/ | 58 | Short rubber | Smooth short rubber | |
| 3024 | " /CF ₃ CH=CF ₂ | 70/30 | 25 | | /6/ | 48 | Rubbery powder | Smooth short rubber | |
| 3025 | CF ₂ -CHCH=CH ₂ /CF ₂ (CF ₂ CFC1) ₂ CF ₂ CO ₂ -CH ₂ -CHCH ₂ | 90/10 | 25 | | /6/ | 60 | - | - | |
| 3026 | " /CF ₂ -CHCF=CH ₂ | 90/10 | 70 | 25 | /6/ | 68 | - | Very short rubber | |
| 3027 | " / " | 80/20 | 70 | 25 | /6/ | 62 | Short rubber | Tough short rubber | |
| 3028 | " / " | 50/50 | 70 | 25 | /6/ | 92 | - | - | |
| 3029 | " / " | 25/75 | 70 | 25 | /6/ | 90 | Tough short rubber | Rubbery sheet | |
| 3030 | CF ₂ -CHCH=CH ₂ | 100 | 70 | 25 | /3/ | 40 | Powder | - | |
| 3012 | CH=CH ₂ / CF ₂ -CHCH=CH ₂ | 50/50 | 20 | 40 | /3/ | 50 | Yellow flakes | - | |
| 3013 | " /CF ₂ CHCF=CH ₂ | 50/50 | 20 | 40 | /3/ | 26 | Brown flakes | - | |
| 3014 | " /CF ₂ -CFC1=CH ₂ | 50/50 | 20 | 40 | /3/ | 83 | Brown flakes | - | |
| 3015 | " /CH ₂ =CHC(CF ₃)=CH ₂ | 50/50 | 20 | 40 | /3/ | 23 | Soft yellow rubber | - | |
| 3016 | homopolymer | 100/0 | 24 | 25 | /3/ | 64 | Yellow plastic | - | |
| 3017 | /CH ₂ =CF ₂ | 40/60 | 24 | 25 | /3/ | 40 | Lt. yellow plastic | - | |
| 3018 | /CF ₂ -CFC1 | 50/50 | 24 | 25 | /3/ | 80 | Black flakes | - | |
| 3019 | /CF ₂ -CF ₂ | 45/55 | 24 | 25 | /3/ | 43 | Yellow chips | - | |
| 3020 | /CH ₂ =CHC(CF ₃)=CH ₂ | 5/95 | 60 | 25 | /3/ | 92 | Soft rubber | Weak crepe sheet | |
| 3021 | / " | 15/85 | 60 | 25 | /3/ | 92 | Short stiff rubber | Stiff crepe sheet | |
| 3023 | / " | 5/95 | 60 | 25 | /3/ | 92 | Soft rubber | Crepe sheet | |
| 3022 | CH ₂ -CH ₂ /CH ₂ -CHC(CF ₃)=CH ₂ | 5/95 | 60 | 25 | /3/ | 96 | Soft sticky rubber | Weak sticky sheet | |
| 3036 | CF ₂ -CHCH=CH ₂ /CF ₂ -C(CH ₃)CH=CH ₂ | 75/25 | 40 | 25-40 | /3/ | 8 | Soft rubber | Short snappy rubber | |
| 3037 | " /CF ₂ -CPCH=CH ₂ | 90/10 | 40 | 25-40 | /3/ | 51 | Short stiff rubber | Tough stiff sheet | |
| 3038 | " / " | 80/20 | 40 | 25-40 | /3/ | 64 | Short stiff rubber | Tough stiff sheet | |
| 3039 | " / " | 50/50 | 40 | 25-40 | /3/ | 70 | - | Tough flexible sheet | |
| 3040 | " / " | 40/60 | 40 | 25-40 | /3/ | 80 | Short tough rubber | Tough stiff sheet | |
| 3041 | /CH ₂ -C(CF ₃)CH=CH ₂ | 75/25 | 40 | 25-40 | /3/ | 51 | Soft rubber | Soft, translucent rubber | |
| 3042 | " / " | 50/50 | 40 | 25-40 | /3/ | 65 | Soft rubber | Soft, snappy rubber | |
| 3043 | " / " | 25/75 | 40 | 25-40 | /3/ | 75 | Soft, weak rubber | Soft, translucent rubber | |
| 3034 | CF ₂ -CH ₂ /CF ₃ CF=CF ₂ | 95/5 | 18-1/2 | 50 | /6/ | 80 | Rubbery powder | Plastic | |
| 3048 | CF ₂ -CFH/CF ₃ -C-CF ₂ | 70/30 | 24 | 50 | /6/ | 47 | Sl. rubbery particles | Flexible plastic sheet | |
| 3049 | " / " | 60/40 | 24 | 50 | /6/ | 60 | Sl. rubbery cramps | - | |
| 3052 | CF ₂ -CH ₂ /CH ₃ CH=CH ₂ | 70/30 | 22 | 50 | /6/ | zero | - | - | |
| 3053 | CF ₂ -CFCP ₂ C1 | 100/0 | 24 | 50 | /6/ | zero | - | - | |
| 3054 | CF ₂ -CF ₂ Cl/CF ₂ -CHCF=CH ₂ | 30/70 | 24 | 50 | /6/ | 26 | Rubber | Snappy rubber | |
| 3055 | " /CF ₂ -CPCH=CH ₂ | 30/70 | 24 | 50 | /6/ | 58 | Hard short rubber | Very short rubber | |
| 3056 | /CH ₂ -CCH=CH ₂ | 30/70 | 24 | 50 | /6/ | 51 | Snappy rubber | Soft rubber | |
| 3057 | /CF ₂ -CFC1 | 30/70 | 24 | 50 | /6/ | 34 | White powder | - | |
| 3058 | " / CH=CH ₂ | 30/70 | 24 | 50 | /7/ | 50 | Brown short rubber | - | |
| 3060 | CF ₃ CCl=CF ₂ | 100/0 | 66 | 25 | /8/ | low | Yellow oil | - | |
| <u>Terpolymers</u> | | | | | | | | | |
| 3035 | CF ₂ -CH ₂ /CF ₃ CF=CF ₂ /CH ₂ -CHOCH ₂ CF ₂ H | 80/10/10 | 18-1/2 | 50 | /6/ | 76 | Very short rubber | Tough leathery sheet | |
| 3044 | " / " / " | 60/36/4 | 17-1/2 | 50 | /6/ | 73 | Soft rubber | Soft rubber | |
| 3045 | CF ₂ -CHCF=CH ₂ /CH ₂ -CCH=CH ₂ /CH ₂ -CHCN | 50/40/10 | 24 | 50 | /9/ | 82 | Soft rubber | Crepe rubber | |
| 3046 | " /CF ₂ -CPCH=CH ₂ /CH ₂ -CHCN | 40/50/10 | 24 | 50 | /6/ | 90 | Sl. short rubber | Crepe short rubber | |
| 3047 | CF ₂ -CHCH=CH ₂ /CH ₂ -CCH=CH ₂ / | 50/40/10 | 24 | 50 | /6/ | 92 | Tough rubber | Crepe short rubber | |

/1/ Recipe: Water 200; Perfluorooctanoic acid 0.75; K₂S₂O₈ 1; Na₂S₂O₈ 0.4; monomer 100; n-hexane 1.32; pH of polymerization medium 7.

/2/ Recipe: Same as recipe /1/, except n-hexane 2.64.

/3/ Recipe: Same as recipe /1/, except no n-hexane.

/4/ Recipe: Acetone 200; benzoyl peroxide 1; monomer 100.

/5/ Recipe: Tetrahydrofuran 200; benzoyl peroxide 1; monomer 100.

/6/ Recipe: Water 200; perfluorooctanoic acid 1; K₂S₂O₈ 1; Na₂S₂O₈ 0.4; monomer 100.

/7/ Recipe: Water 200; HgNR 5; K₂S₂O₈ 1; Na₂S₂O₈ 0.4; pH of polymerization medium 7.

/8/ Recipe: CF₃CCl=CF₂ 8.5 g.; Freon 11k 5 cc.; WF₃ 0.12 g. (in 45 cc.); Sealed in stainless steel bomb and stood for 66 hrs.

/9/ Recipe: Water 200; Perfluorooctanoic acid 1; K₂S₂O₈ 1; Na₂S₂O₈ 0.4; pH of polymerization medium 7.

/10/ Recipe: The combined molar ratios of these polymers will be reported when the analytical data are predictable.

/11/ Recipe: All the samples tanned on mill at 25°C., except runs 3024, 3025 and 3026 which tanned at 50°C.

TABLE II
ARCTIC RUBBER SCREENING TEST

| Run No. | Monomer Structure Copolymer | Molar Ratio Combined Charged | % Cons. | Appearance of Sample Before Milling /1/ | | Gehman Stiffness (cc.) | Vol. of Increase Tensile Modulus Tensile Modulus Tensile Modulus (cc.) /2/ | Tensile Modulus (cc.) /3/ | Sample Condition After Milling |
|---------|--|------------------------------------|-----------|--|---------------|--------------------------|--|---------------------------------|-----------------------------------|
| | | | | 12 | 10 | | | | |
| 1999 | CF ₂ -OFC1/CF ₂ -CHOF-CH ₂ | 50/50 | 13/87 | 49 | Rubber | -16.4 | -24.0 | -37.6 | 15 |
| 1971 | CF ₂ CF-CF ₂ /CF ₂ -CHOF-CH ₂ | 25/75 | Loss of F | 43 | " | Short rubber | -12.9 | -18.8 | -23.3 |
| 1972 | " /CH ₂ -COH ₂ -CH ₂ | 25/75 | Loss of F | 64 | " | Soft rubber | +19.8 | -1.0 | -11.7 |
| 1973 | CH ₂ -OHC1/ | 25/75 | 20/80 | 95 | " | Slightly tough rubber | + 9.0 | -7.8 | -15.3 |
| 1959 | CF ₂ -OHC1/CF ₂ -OHCOP=CH ₂ | 10/90 | 1.5/98.5 | 62 | " | Slightly short rubber | -11.3 | -20.6 | -23.8 |
| 1960 | CF ₂ -OHC1/ | 25/75 | 2/98 | 50 | " | " | -15.4 | -21.1 | -24.7 |
| 1961 | CF ₂ CCl=CH ₂ / | 10/90 | 11/89 | 66 | Snappy rubber | Crepe rubber sheet | + 4.2 | -10.3 | -14.3 |
| 2001 | CF ₂ -OHCOP=CH ₂ /CF ₂ -OFC1=CH ₂ | 95/5 | - | 87 | Short rubber | Crepe rubber sheet | -14.1 | -24.1 | -27.1 |
| 2000 | " / " | 90/10 | - | 84 | " | Soft rubber | -15.1 | -24.3 | -27.3 |
| 1984 | " / " | 80/20 | - | 70 | Rubber | Crepe rubber sheet | -15.2 | -23.5 | -25.5 |
| 1983 | " / " | 75/25 | - | 84 | Rubber | " | -20.4 | -24.4 | -27.1 |
| 1982 | " / " | 60/40 | - | 78 | " | " | - 6.7 | -23.9 | -24.5 |
| 1986 | " / " | 50/50 | - | 76 | " | Tough crepe rubber sheet | -17.4 | -26.9 | -29.1 |
| 1985 | " / " | 40/60 | - | 80 | " | " | -15.3 | -27.3 | -29.5 |
| 1976 | /C1(CF ₂ CFCl) ₂ CF ₂ CO ₂ CH ₂ CH=CH ₂ | 79/21 | 95.5/4.5 | 35 | " | Kubbry crepe sheet | - 8.0 | -14.3 | -17.0 |
| 1977 | " / " | 90/10 | 97.5/2.5 | 49 | " | " | -11.5 | -20.0 | -23.1 |
| 2002 | CF ₂ -OPOH=CH ₂ /CH ₂ -COH ₂ -CH ₂ | 80/20 | 69/31 /3/ | 99 | " | Soft rubber | -26.8 | -30.7 | -32.8 |
| 2003 | " / " | 75/25 | 65/35 /3/ | 91 | " | " | -23.8 | -29.3 | -32.0 |
| 2004 | " / " | 60/40 | 15/85 /3/ | 99 | " | Rubber | - 2.8 | -19.3 | -24.5 |
| | <u>Terepolymers</u> | | | | | | | | |
| 1978 | CF ₂ -OCHOF-CH ₂ /CF ₂ =OCH=CH ₂ /CF ₃ CCl=CH ₂ | 50/40/10 | - | 72 | Rubber | Rubbery crepe sheet | -15.3 | -22.5 | -23.9 |
| 1979 | " / " /CH ₂ -CHOCF ₂ CF ₂ H | 50/40/10 | - | 56 | Soft rubber | Short rubber | -26.7 | -32.5 | -34.2 |
| 1980 | " / " /C1(CF ₂ CFCl) ₂ CF ₂ CO ₂ - CH ₂ CH=CH ₂ | " | - | 60 | Rubber | Slightly tough rubber | -15.6 | -22.3 | -25.6 |
| 1981 | " / " /CH ₂ -COH ₂ -CH ₂ | 50/40/10 | - | 78 | Rubber | Kubbry crepe sheet | -20.9 | -25.4 | -27.3 |
| 1964 | " /CH ₂ -OCH ₂ -CH ₂ /CF ₂ -OCHCl | 40/40/20 | - | 74 | Soft rubber | Soft rubber | -20.5 | -27.2 | -29.2 |
| 1963 | " / " /CP ₃ CCl=CH ₂ | 40/50/10 | - | 62 | hubber | Rubbery crepe sheet | -17.0 | -23.4 | -25.9 |

/1/ All the samples banded on mill at 25°C.

/2/ Mold times unless otherwise noted are 10 minutes. Longer periods are totals of individual 10 minute periods.

/3/ Reason for unexpected analytical results not determined.

TABLE III
COPOLYMERS OF CF₂-CH₂/CF₂-CFCF₂Cl

| Run No. | <u>3050</u> | <u>3051</u> | <u>3059</u> | <u>3061</u> |
|---|---------------------|---------------------|---------------------|---------------------|
| Molar Ratio of CF ₂ -CH ₂ /CF ₂ -CFCF ₂ Cl: | | | | |
| Charged Combined | 70/30 75.5/24.5 | 60/40 68.4/31.6 | 50/50 64.8/35.2 | 25/75 55.2/44.8 |
| Polymerization Conditions | | | | |
| Time, hrs. | 22-1/2 | 22 | 69 | 23 |
| Recipe | /1 | /1 | /1 | /1 |
| % Conversion | 88 | 77.5 | 66.7 | 34 |
| Appearance of Sample: | | | | |
| Before milling | White Rubber | White Rubber | White Rubber | Sl. hard Rubber |
| After milling /2/ | Crepe rubbery sheet | Crepe rubbery sheet | Crepe rubbery sheet | Crepe rubbery sheet |
| Torsional Modulus, psi | 180 | 169 | 168 | 178 |
| Gehman values, °C. /3/ | | | | |
| T ₂ | +3 | +9 | +11 | +13 |
| T ₅ | -3 | +3 | +5 | +10 |
| T ₁₀ | -6 | 0 | +3 | +9 |
| T ₁₀₀ | -16 | -9 | -6 | +4 |
| Resilience (Bayshore) | 7 | 10 | 5 | - |
| "Eeso Turbo Oil 15" | | | | |
| 18 hrs. at 77°F. wt. % increase | 35 | 19 | 47.8 | - |
| 1 hr. at 600°F. | | Partially soluble | | |

/1/ Recipe: Water 150; C₈ Telomer Acid 0.75; Na₂HPO₄·7H₂O 3;
K₂S₂O₈ 0.75; Monomer 50-60

/2/ All samples banded on mill at 25°C.

/3/ All samples were molded at 300°F.